

SCIENCE FOR GLASS PRODUCTION

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GERMANATE LEAD-TELLURITE GLASSES FOR OPTICAL LIGHT FILTERS

G. E. Rachkovskaya^{1,2} and G. B. Zakharevich¹

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Glass formation, crystallizability, physical-chemical properties, and spectral characteristics of $\text{GeO}_2\text{--TeO}_2\text{--B}_2\text{O}_3\text{--PbO}$ glasses were studied. The structural properties of the glasses were investigated and the coordination transitions of boron and germanium ions in the glass structure were found. A nonlinear dependence of the physical-chemical properties of the glasses on their composition and structure was found and interpreted as a manifestation of “borate and germanate” anomalies in the glasses. The optical absorption spectra of the glasses were found to be characterized by a steep fundamental absorption edge at the boundary of the visible and UV regions of the spectrum, which makes it possible to recommend the glasses for use as light filters cutting off the UV region.

Key words: glass, glass formation, crystallization, physical-chemical properties, structure, absorption spectra, light filters.

Germanate lead-tellurite glasses synthesized on the basis of the glass-forming system $\text{GeO}_2\text{--TeO}_2\text{--B}_2\text{O}_3\text{--PbO}$ are of scientific and practical interest for optoelectronics and optical laser engineering as high-refractivity glasses that transmit IR radiation and cut off the UV region from the visible spectrum. Because of the high cost of germanium and its compounds germanium dioxide is not used in mass-produced glasses.

However, because germanium dioxide imparts to glass a number of high physical-chemical, optical, and operational properties interest in germanate glass has increased dramatically, and special-purpose glasses are now synthesized on the basis of germanium dioxide. Such glass is used for fiber lasers [1], active media in fiber-optic communication lines [2], and light filters [3, 4].

Tellurium-containing glasses are also distinguished by good IR-transparency and a high refractive index. Combining the dioxides GeO_2 and TeO_2 in glass compositions makes it possible to synthesize new glasses with high optical-spectral properties for use in optical instrument building as, for example, optical light filters cutting off the UV region of the spectrum.

We shall examine the results obtained in a study of glass formation, crystallizability, physical-chemical properties,

structural characteristics, and spectral characteristics of $\text{GeO}_2\text{--TeO}_2\text{--B}_2\text{O}_3\text{--PbO}$ glasses.

The composition limits of the experimental glasses and the glass-formation region at temperature 950°C are shown in the glass-formation diagram (Fig. 1). As one can see from the diagram these boundaries coincide, i.e., at 950°C all syn-

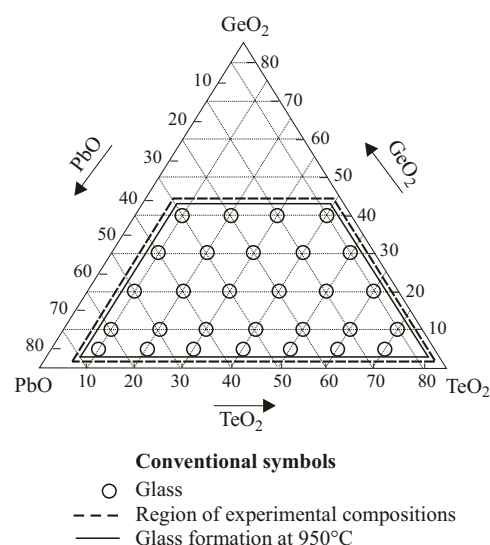


Fig. 1. Diagram of glass formation in the system $\text{GeO}_2\text{--TeO}_2\text{--B}_2\text{O}_3\text{--PbO}$ at 950°C (the B_2O_3 molar content is constant and equals 15%).

¹ Belorussian State Technological University, Republic of Belarus, Minsk.

² E-mail: rach_halina@mail.ru.

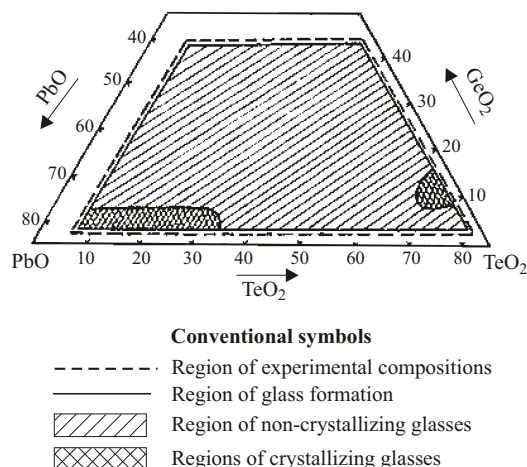


Fig. 2. Crystallizability of $\text{GeO}_2\text{--TeO}_2\text{--B}_2\text{O}_3\text{--PbO}$ glasses (the B_2O_3 content is constant and equals 15%).

thesized compositions form melts which transform into glass on cooling. The synthesized glasses are characterized by the glassy-state stability, which is due to the oxides introduced in the glass composition. First and foremost, the glasses contain two typical glass formers: germanium dioxide and boric anhydride.

Tellurium oxide is a conditional glass former, one of a class of compounds which unlike classic glass formers (SiO_2 , B_2O_3 , P_2O_5 , GeO_2) do not form glass in pure form [5]. This is due to the asymmetric spatial structure of TeO_2 resulting from the unidirectionality of the Te--O bonds. Small additions of other oxides lead to the formation of the ionized structural complexes $\text{TeO}_3/2\text{O}^-$ which have a high possibility of shifting relative to one another and thereby forming an infinite, spatially disordered, structural network of glass [6]. In glasses lead oxide can play a dual role, acting as a modifier in the form of $[\text{PbO}_6]$ groups and a glass former in the form of $[\text{PbO}_4]$ groups of the structural network of the glass [7–9]. Apparently, the stability of the glasses in the experimental system is explained by the creation of a single spatial network based on two or more glass-forming oxides.

The study of the crystallizability of the experimental glasses confirmed that practically all of the glasses synthesized are stable against crystallization (Fig. 2). The exceptions were small sections adjoining the PbO--TeO_2 and PbO--GeO_2 sides of the Gibbs concentration triangle in the molar content range 5, 10% GeO_2 . Very slight indications of crystallization were observed in this composition region during heat treatment: skinning on the surface and a thin crystalline film in the temperature range 350–490°C with molar content 5% GeO_2 and 490–580°C with 10% GeO_2 . As temperature increased these very slight crystal formations melted, forming a pure melt.

The stability of the glasses against crystallization can also be explained by the high polarizability of the cations Te^{4+} , Ge^{4+} , and Pb^{2+} . The high polarizability of these cations is responsible for the high directionality of the Te--O , Ge--O ,

and Pb--O bonds, as a result of which during crystallization the rearrangement of the structural elements connected by directed bonds is impeded to a greater extent than in the case where the bonds are not directed.

The physical-chemical properties of the glasses were studied: softening onset temperature $t_{s,0}$, CLTE, microhardness, and density. A series of glasses with constant molar content 10, 20, and 40% GeO_2 with equimolar substitution of lead oxide for tellurium dioxide was studied. The dependence of these properties on the chemical composition of the glasses is shown in Fig. 3. It should be noted that this dependence is not linear. Inflections are present in the concentration curves of the softening onset temperature and the CLTE. These inflections were interpreted as structural rearrangements, in all probability of the coordination type, occurring in the glass when its chemical composition changes.

The synthesized glasses are distinguished by easy melting. The softening onset temperature for this series of glasses varies from 330 to 390°C and the CLTE from 77 to $125 \times 10^{-7} \text{ K}^{-1}$ depending on the chemical composition of the glass. The microhardness of the glasses is in the range 1100–1650 MPa and increases with equimolar substitution of TeO_2 for PbO . Low microhardness is characteristic for glasses with high lead oxide content. The density of the experimental glasses increases as the lead oxide concentration, lying in the range 4300–6200 kg/m^3 .

The structural features of the glasses were studied by means of IR-spectroscopy. The IR absorption spectra of the experimental glasses were obtained in the frequency range 1400–400 cm^{-1} . Figure 4 displays a series of glasses with constant molar content 10% GeO_2 and equimolar substitution of TeO_2 for PbO . Analyzing the IR-spectra of this series of glasses, it can be concluded that they are all characterized by strong absorption bands in the ranges 1340–1200 cm^{-1} and 800–600 cm^{-1} . The absorption bands in the high-frequency region of the spectrum with peaks in the range 1340–1200 cm^{-1} are due to triply coordinated boron groups $[\text{BO}_3]$ which are either isolated or components of isolated meta- and pyroborates containing boroxyl rings [10, 11]. It should be noted that these absorption bands correlate with the content of lead oxide PbO , whose concentration changes at the expense of tellurium dioxide, in the glass. Thus, the peak in the absorption band in high-lead glass with molar content 75% PbO (no TeO_2) lies at 1200 cm^{-1} . The $[\text{BO}_3]$ group in the form of boroxyl rings is present in the structure of this glass. As the PbO content decreases and TeO_2 content increases the center of gravity of this band gradually shifts into the short-wavelength region of the spectrum from 1200 to 1240 cm^{-1} , after which a second peak at 1280 cm^{-1} appears in the contour of this band. This latter peak gradually shifts into the short-wavelength region of the spectrum to 1340 cm^{-1} , attesting to the accumulation of the polymerized $[\text{BO}_3]$ groups.

The absorption band in the region 1035–1080 cm^{-1} is due to antisymmetric stretching vibrations of tetrahedrally

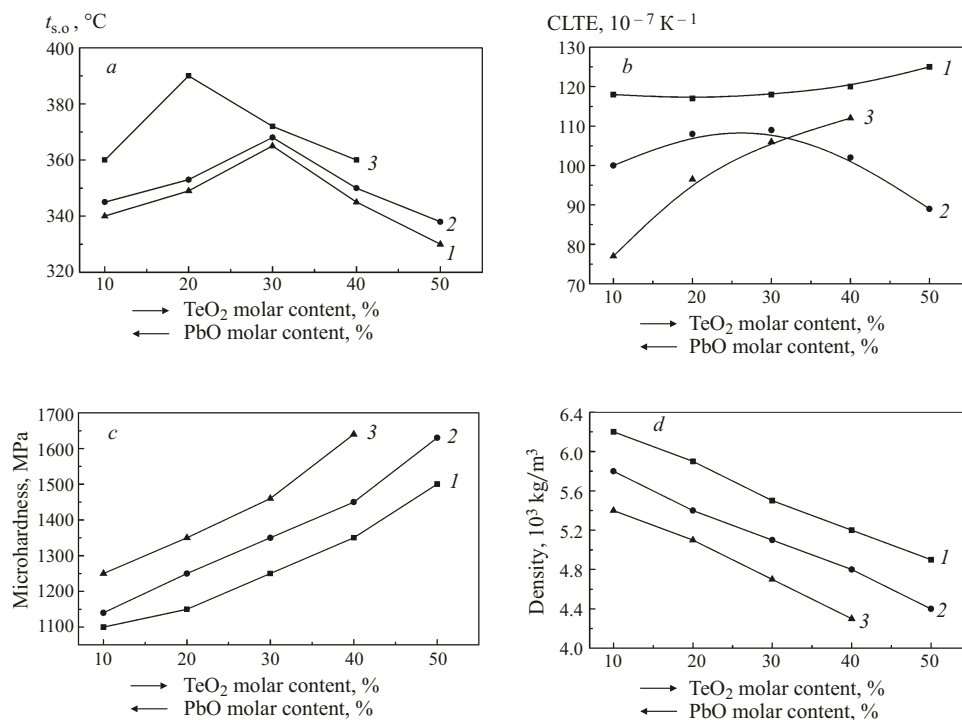


Fig. 3. Dependence of the physical-chemical properties of the glasses — softening onset temperature (*a*), CLTE (*b*), microhardness (*c*), density (*d*) — on the composition with equimolar substitution of PbO for TeO₂: 1, 2, 3) GeO₂ molar content 10, 20, and 40%, respectively.

coordinated boron. The [BO₄] groups in the structure of the glasses appear at molar content 20% TeO₂ (the presence of extrema in the composition–property curves).

The second strong absorption band in the region 600–800 cm⁻¹ with an absorption peak at 710 cm⁻¹ is characteristic for an octahedrally coordinated germanium ion [12, 13]. This band changes when tellurium dioxide is introduced into the glass composition. Its contour broadens as a result of the appearance of a second absorption peak at 670–680 cm⁻¹, which attests to the formation of tellurium ions in the triply coordinates state [14]. The position of the peak in this band in the spectrum remains stable at all TeO₂ concentrations in the glass. Therefore, it can be supposed that the coordination state of the tellurium ions in the experimental glasses remains unchanged irrespective of the TeO₂ concentration.

The absorption band in the range 870–920 cm⁻¹ is due to the [GeO₄] tetrahedra, broadening appreciably with increasing TeO₂ concentration; here, one can talk about the accumulation of [GeO₄] groups due to a coordination transition of [GeO₆] into [GeO₄]. There are no absorption bands for the lead ions in this region of the spectrum, so that the coordination state of the lead ions can only be judged indirectly — according to the effect of lead on the change of the coordination state of boron and germanium ions.

Evidently, a change of the coordination state of these ions gives rise to a sharp change of the physical-chemical properties of the glasses and, in consequence, the appearance of extrema in the composition–property curves. The nonlinear dependence of the properties of the glasses on the glass composition can be explained by coordination transitions of

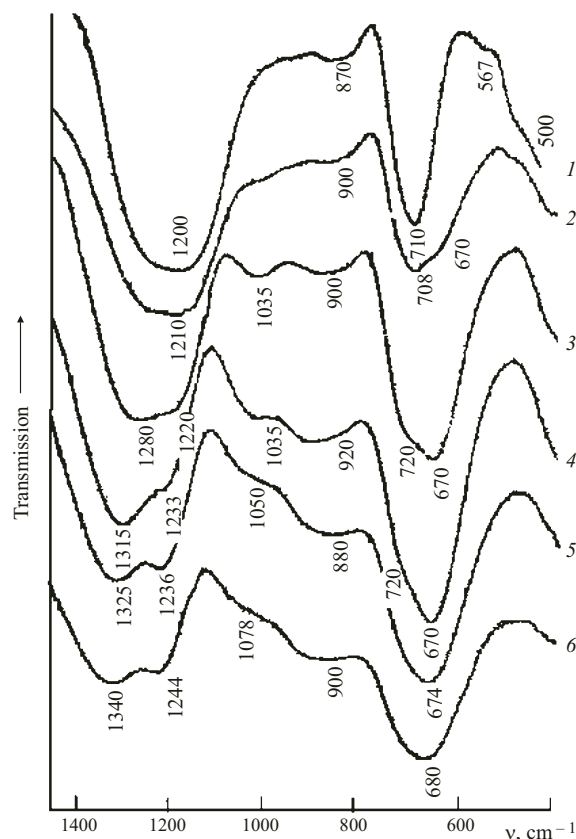


Fig. 4. IR absorption spectra of glasses with equimolar substitution of PbO for TeO₂ and constant GeO₂ molar content, %: 1) no TeO₂, PbO – 75; 2) TeO₂ – 10, PbO – 65; 3) TeO₂ – 20, PbO – 55; 4) TeO₂ – 30, PbO – 45; 5) TeO₂ – 40, PbO – 35; 6) TeO₂ – 45, PbO – 30.

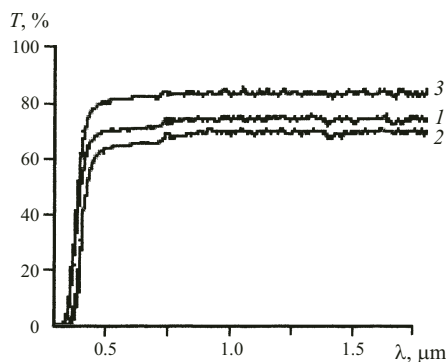


Fig. 5. Optical transmission spectra (T) of glasses with TeO_2 molar content 10 (1), 30 (2), and 50% (3) (the GeO_2 molar content is constant and equals 10%); $d = 2$ mm.

the boron and germanium ions in the structure of the glasses. Apparently, here there are both “borate” and “germanate” anomalies, which manifest in the special behavior of the curves of the physical–chemical properties. These curves can be explained by the changes of the coordination state of the boron and germanium ions in the structure of the glass.

The optical transmission spectra in the UV and near-IR regions of the spectrum (0.30 – 1.75 μm , Fig. 5) were investigated. The optical transmission spectra of the experimental glasses are characterized by a steep fundamental absorption edge at the interface of the UV and visible regions of the spectrum; this is an important criterion for evaluating the glasses with respect to their use for optical cut-off light filters. The optical transmission spectra of the glasses characterize the dependence of the transmission coefficient on the wavelength of the light. The wavelength at which the transmission of the 2 mm thick samples equals 50% is 395 nm for these glasses. The spectral range where the transmission increases from 10 to about 90% is about 80 nm. It should be noted that the optical transmission of the glasses depends on their chemical composition. The transmission of the high-tellurite glasses (GeO_2 molar content is 10%) is about 90% (Fig. 5, curve 3). An equimolar substitution of GeO_2 for TeO_2 initially decreases the transmission of the glasses (curve 2), after which the transmission increases (curve 1) as the GeO_2 molar content increases to 40% (10% TeO_2). Tellurium dioxide has the strongest effect on the optical transmission of the glasses. This is probably because the tellurium ions are more highly polarized than the germanium ions. The studies show that the experimental glasses are transparent in the indicated wavelength range and have a steep optical absorption edge at the interface between the visible and UV regions of the spectrum.

In summary, this research has led to the development of new germanate lead-tellurium glasses based on the GeO_2 – TeO_2 – B_2O_3 – PbO system. Glass formation, crystallizability,

the physical-chemical properties, and the spectral properties were studied for the glasses. The structural particulars of the glasses were studied and coordination transitions of the boron and germanium ions were found in the glass structure. It was established that the physical–chemical properties of the glasses show a nonlinear dependence on their composition and structure, interpreted from the standpoint of the manifestation of “borate and germanate” anomalies in the glasses. The optical absorption spectra of the glasses are characterized by a steep fundamental absorption edge on the interface of the visible and UV regions of the spectrum, which makes it possible to recommend these glasses for use as light filters cutting off the UV region.

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